Oak Ridge National Laboratory

Project ID: Bat439

Silicon Deep Dive: Silicon-Based Slurries and Electrodes

Beth L. Armstrong
Materials Science and Technology Division
Oak Ridge National Laboratory

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Overview

Timeline

- Start October 1, 2017
- End: September 30, 2020
- Percent Complete: 89%

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

Budget

- Funding for FY20: $3000K

Partners

- Argonne National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Pacific Northwest National Laboratory
- *Academic Partners*: University of Tennessee, UMass-Boston, Western Michigan University, University of Illinois-Chicago, University of California

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Relevance

Objective: Understand and control silicon surface chemistry to enable effective incorporation into electrochemical cells

- The **Silicon Deep Dive Next Generation Anode Program** addresses the cost and performance issues preventing the inclusion of silicon into a commercial lithium-ion cell
  - Elemental silicon can theoretically store > 3500 mAh/g and presents a pathway to less than $125/kWh$_{use}$
- Fundamental challenges being addressed include:
  - In order to meet milestones, acceleration of materials - processing relationships need to be understood
  - Stability in the electrochemical cell

Milestones and Activities

FY19Q3 Demonstrate the utility and limitations of anode pre-lithiation in a full cell configuration; extend cycle life of silicon-based baseline electrode by at least 10%. (***Completed 06/19***)

FY19Q4 Construct and evaluate cells based on optimizing lithium inventory, binder, electrolyte formulation, and testing protocol to achieve a 300 Wh/kg cell design based on BatPaC modeling. (***Completed 11/19***)

FY20Q1 Evaluate two new binder - slurry – silicon laminate combinations that lead to improved stability and a 15% improvement in performance compared to baseline for a high silicon-loading (>60%) electrode (***Completed 12/19***)

FY20Q2 Assess and evaluate multiple surface driven coatings that utilize a multivalent surface substitution. Develop an understanding of the formation mechanism on the cycling stability of the underlying silicon electrode; propose a mechanism of formation. (***Completed 2/20***)

FY20Q3 Assess the stability of electrode level silicon baseline materials on cycling and determine the range of species that solubilize and leach into the electrolyte. (***on-going***)

FY20Q4 Combine the advancements made over various aspects of the silicon electrode by the Silicon Deep Dive team evaluate them at the full system level and optimize a best full cell with a commercial cathode that using BatPaC can be determined to deliver > 350 Wh/kg for 120 cycles; Evaluate the energy fade on standing for 2 mos and demonstrate an improvement over baseline of 20%. (***on-going***)

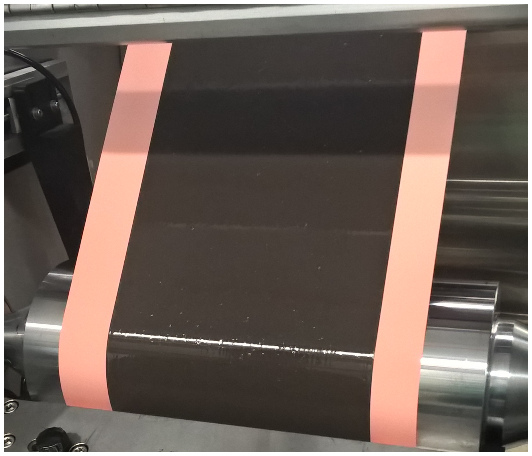
FY20Q4 Have published a document that will enable other research and development groups to analyze stability of the SEI on a silicon-based anode, thus enabling developers or researchers to continually improve silicon cell stability (*joint milestone with the SEISta*). (***on-going***)

Utilizing colloidal and processing expertise for the development of coatings, additives, and processes to modify and stabilize relevant interfaces

Approach and Overview

Electrode Homogeneity = Improved Performance

- Liquid-Solid Interfaces Control Homogeneity and Electrode Performance
- Team Effort Utilizing Expertise at Partner Labs
  - Consistent Protocols (materials, processes)
    - Develop understanding of how process impacts properties
  - Rheology of electrode formulation
    - Structure during processing, electrode formation and drying
  - Powder Surface Modification
    - Additives to Control Attractive Forces at Powder Surfaces (Organic and/or Inorganic)



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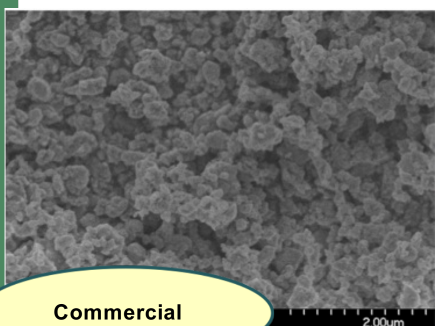
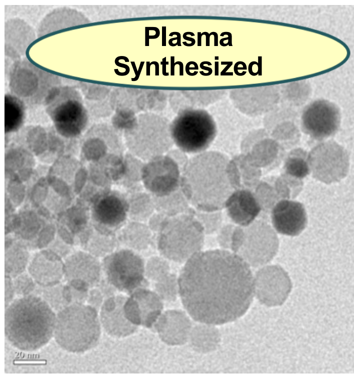
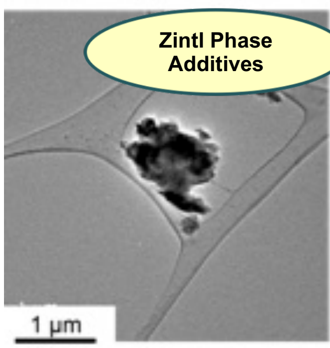
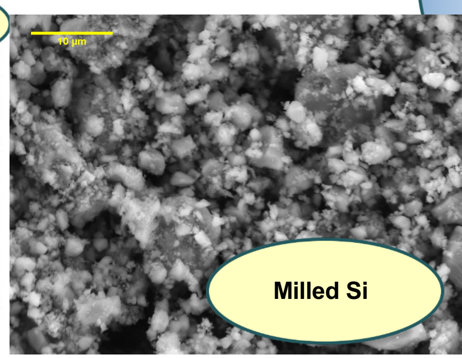
Approach and Overview

Accelerate routes to good electrodes through science









Q4 milestone

Good electrodes vs bad

Characterization

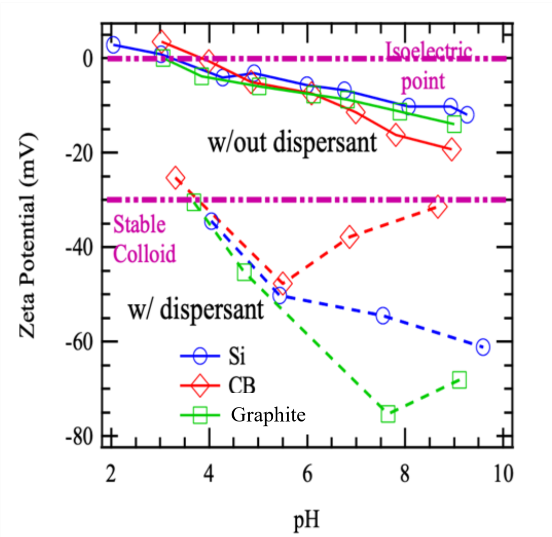
Zeta Potential
Surface chemistry/spectroscopy
Rheology
RAMAN
FTIR

CAMP

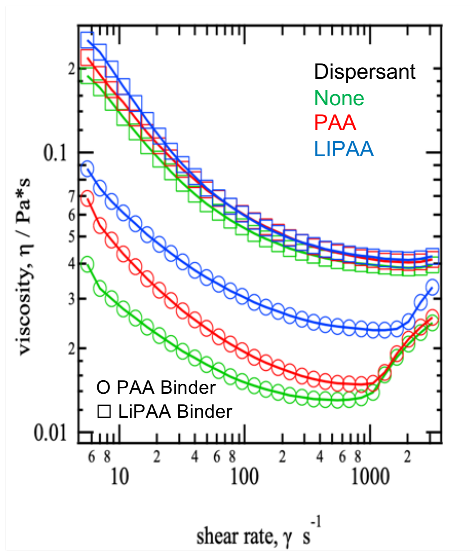
Electrode Scale up

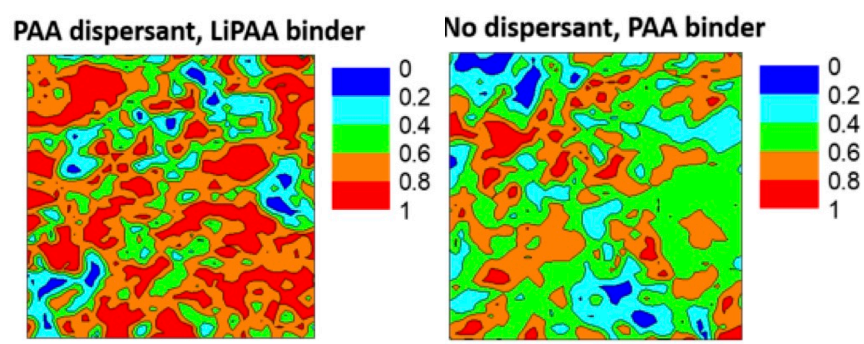
Approach and Overview

Demonstrated controlling slurry interactions leads to improved capacity and performance



Dispersant = 1,200 MW PAA





Control surface charge to enable dispersion. Carbon black sensitive to pH & agglomeration.

Dispersant & binder chemistry changes flow behavior.

Dispersant/binder chemistry alters electrode homogeneity.

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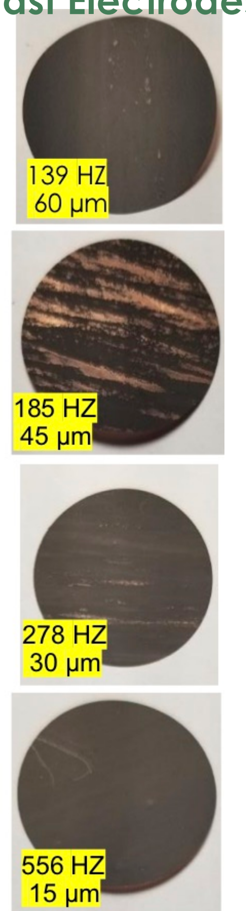
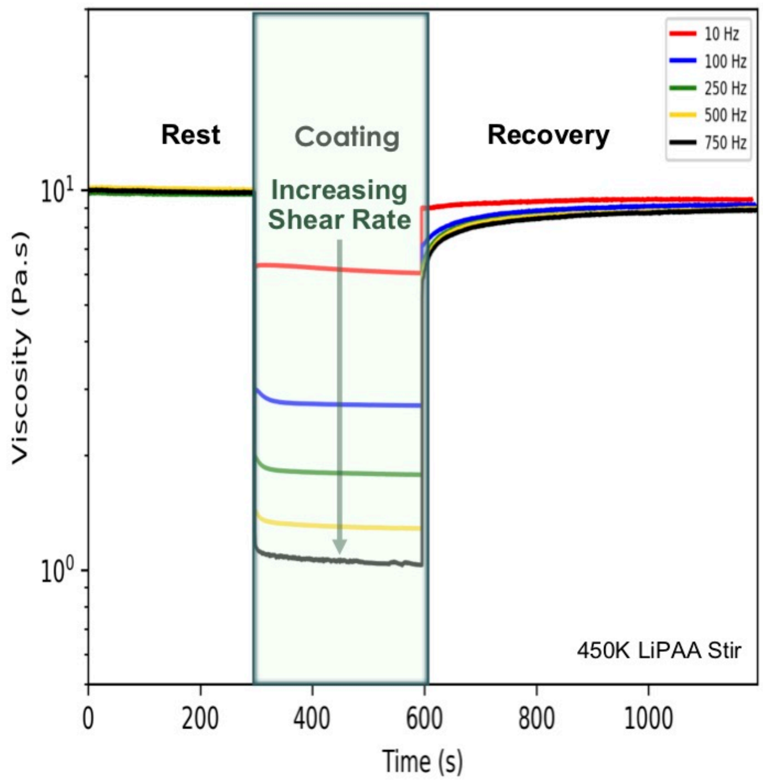
Stress during casting is directly related to electrode homogeneity

Cast Electrodes





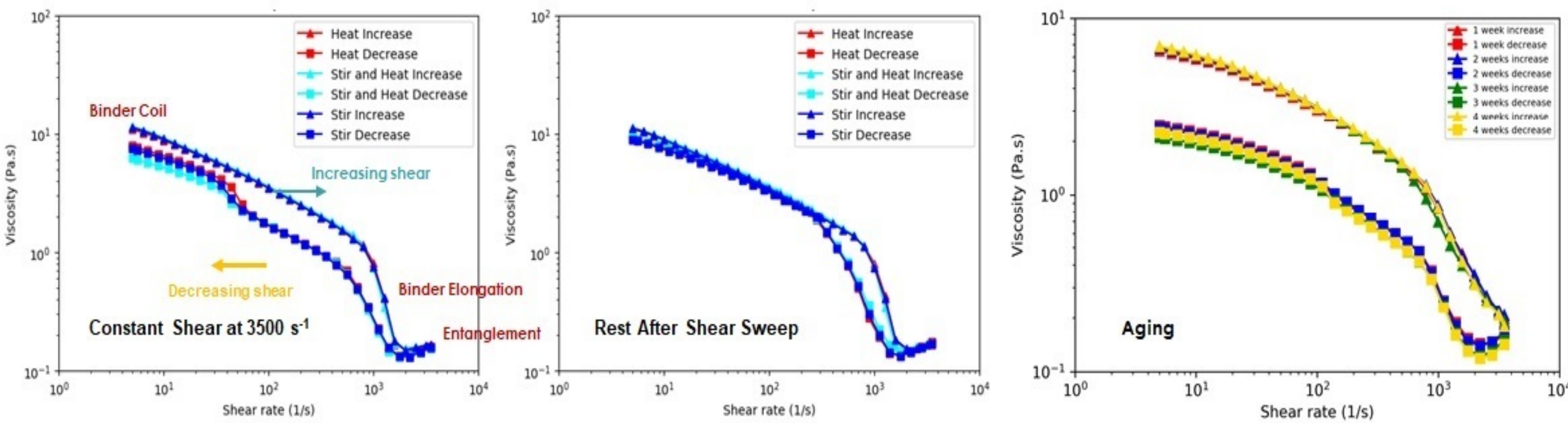
Time Dependent Structural Regeneration After Shearing

The larger the stress, the longer the cast electrode recovery time

Recovery time allows for reorganization of the electrode architecture

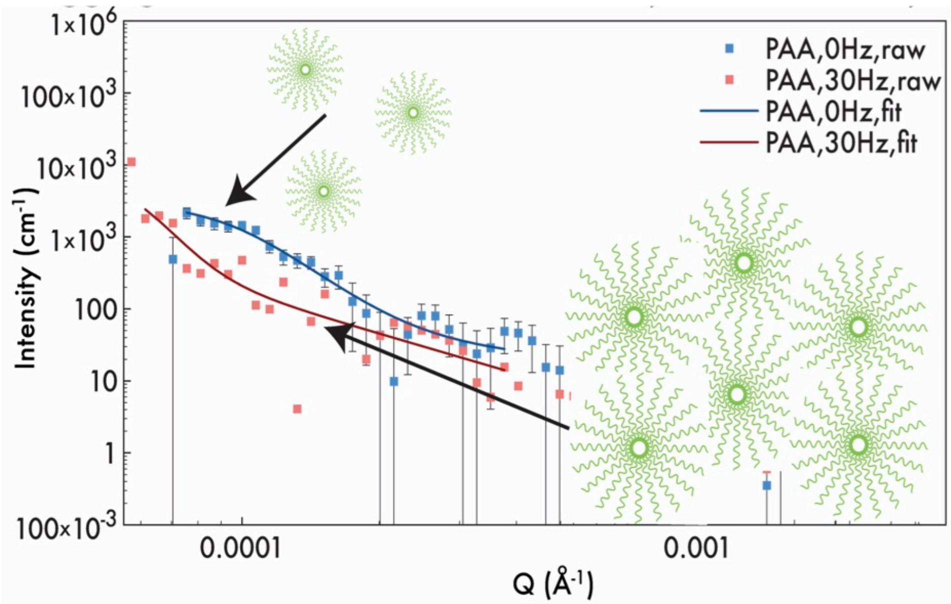
Teaches to a new direction to cast electrode

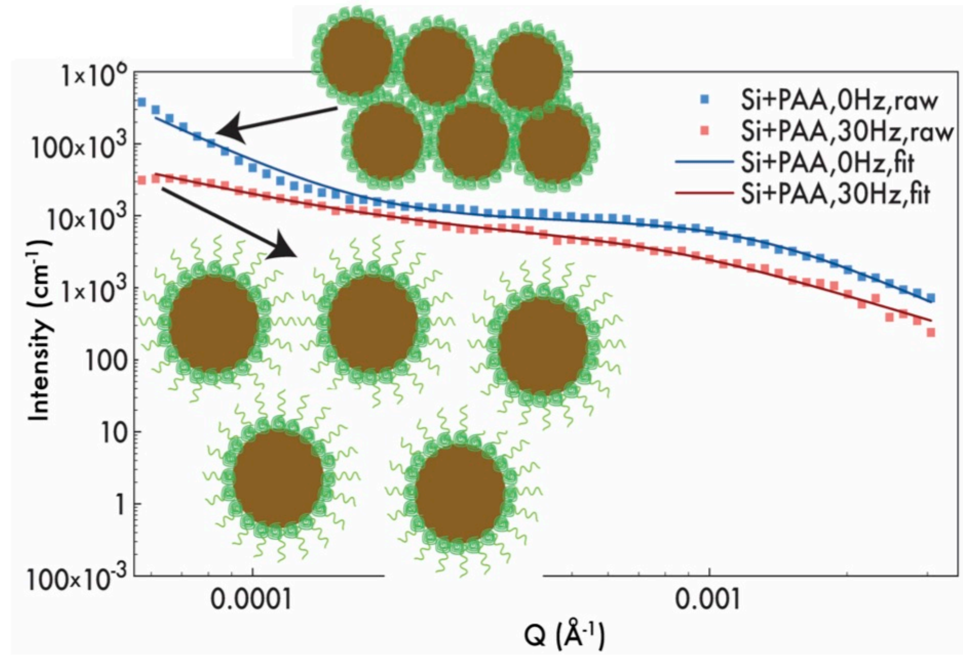
Rheology of the solution method influences electrode homogeneity



- Mixing changes the binder structure and resulting flow behavior
- Higher shear rates are required to elongate binder
- Teaches toward novel or different processing approaches

Si surface changes the aggregation and structure of binder in solution

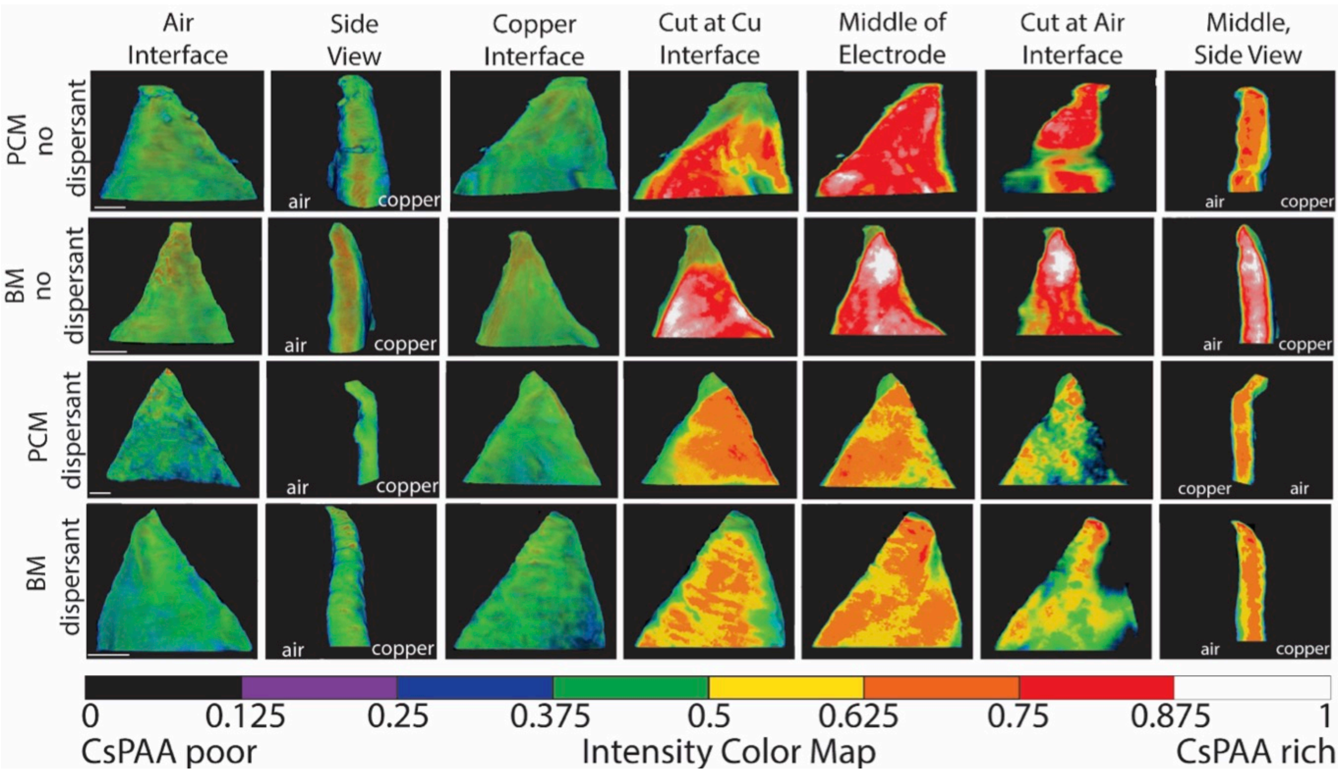




Si causes binder to collapse upon itself and limits extension even with shear

Introducing functionalization to Si changes this aggregation and resulting electrodes

X-ray nanotomography reveals electrode heterogeneity

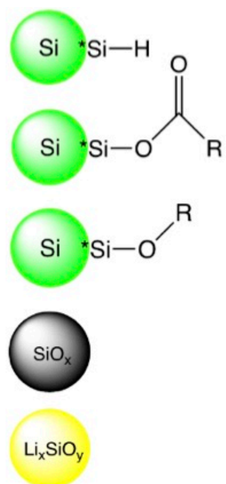


Bright spots correspond to high binder concentrations

Carbon black segregation to surface

Optimizing mixing and slurry chemistry provides a pathway to improve electrode homogeneity

Functionalization of Si surface with experimentally validated stable chemical moieties.



(Silicon Hydride) Reactive

(Silyl Ester) Reactive

(Silyl Ether) Stable

(Geminal OH) Reactive

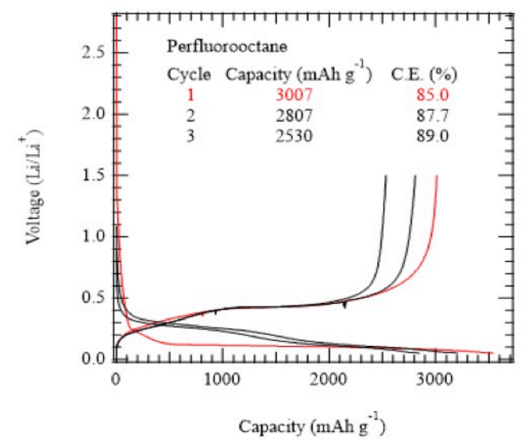
(Linear OH) Stable

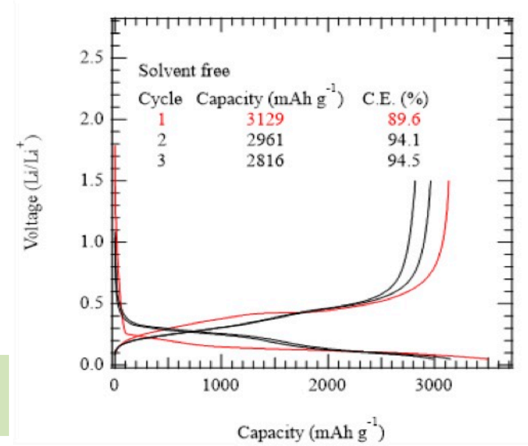
(Li_2SiO_3) Reactive

(Li_4SiO_4) Stable

Purposely breaking Si particles in presence of sacrificial additive that will functionalize Si surface with stable chemical species

0.2-0.5 kg scale/run





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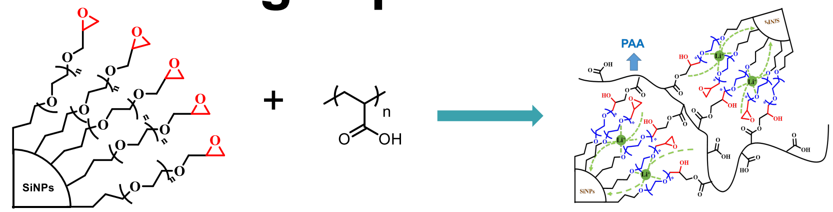
SiNPs surface functionalization changes particle-binder interaction

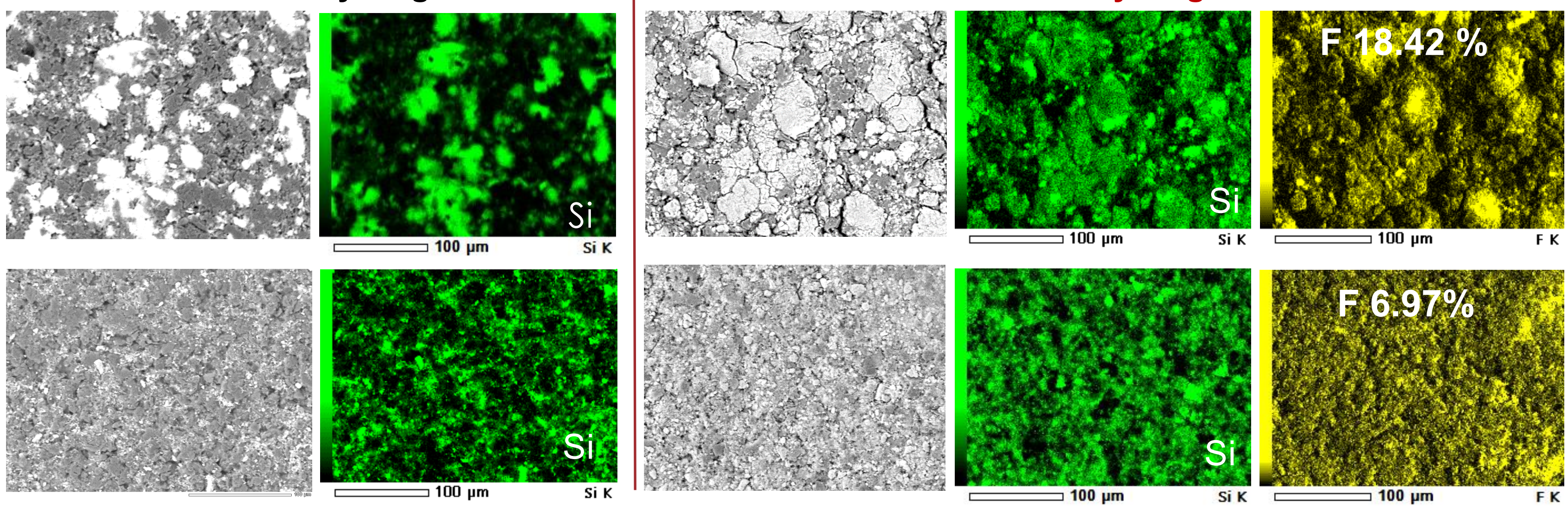


Si-C3-(EO)$_n$-Epoxy

Before cycling **After cycling**

Untreated SiNPs Anode

Epoxy -SiNPs Anode

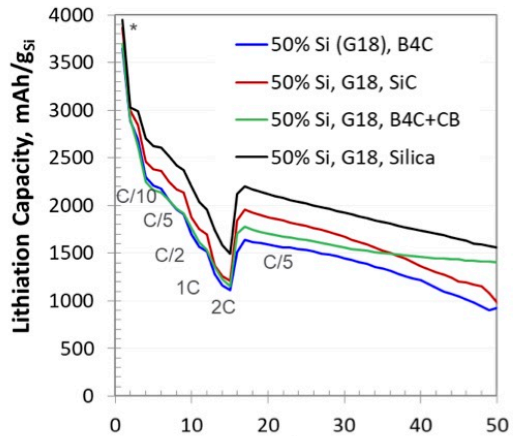


- Epoxy surface group reacts with the carboxylic acid on the PAA binder *via* a ring-opening reaction forming a covalent bond between the Si nano-particles and the polymer binder.
- The formation of covalent bond promotes the adherence of Si particles thus enhances the electrode integrity.

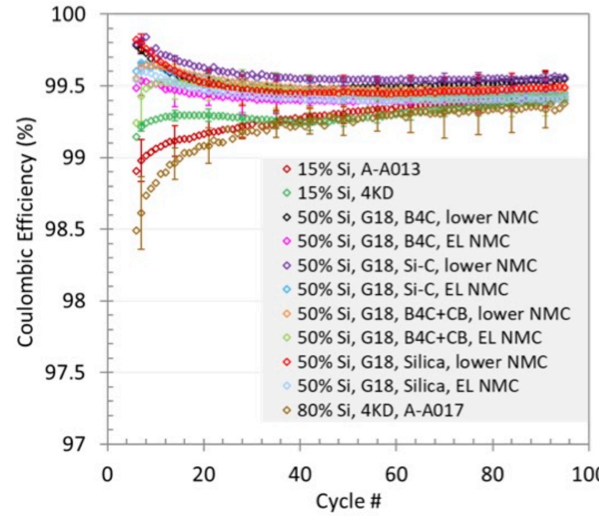
Inert carbon-free refractory materials as additives improve electrodes

Carbon-based conductive additives have high surface area that lead to large 1st cycle irreversibly capacity losses.

Material	Resistivity (25°C), Ohm-cm
Copper	10^{-6}
Carbon	<0.1
Boron carbide	0.1-10
Silicon carbide	10^{2}-10^{5}
Silica	10^{18}



Coin cells, vs. Li
~2 mAh/cm^2
*Formation cycles
Gen2+10wt.% FEC



Cells made with wide range of additives (conductor-to-insulator) all showed very similar capacity, rate performance, and cycle life – even the cell with silica

Comparisons to previous silicon baseline electrodes with 15 & 80 wt.% Si with carbon/graphite show nearly identical fade rate vs matched NMC532

Responses to Reviewers' Comments

- **Several reviewers commented on the advances individual components made versus baseline silicon cycling, including new electrolyte additives, silicon coatings, or LHCE electrolytes, however the presentation did not appear to discuss efforts to bring these individual advances together to assess them as a systems against baseline.**
  - Thank you for the question. As stated, the program was initiated and designed to evaluate several electrode components and assess their properties and performance. For instance initial studies focused on several different binders but for program baseline consistency, the field was down selected to LiPAA based electrodes on electrode quality and relative performance. Efforts trying to understand LiPAA on electrode structure in the system have continued (led by B. Armstrong (ORNL), L. Zhang (ANL)). Overall, at the end of FY18, our Q4 milestone brought together several advances to evaluate their symbiotic properties and help evaluate deficiencies in the materials program. For instance, higher cell stack pressure and Mg-based electrolyte additives, had a >10% improvement over baseline with extended cycling. BatPaC modeling of the data then identified electrode consistency as an area of needed effort that was extended into FY20 milestones.
- **A reviewer asked why does the 15% Si / 73% Gr cell degrade to gave the same performance as a 70% silicon cell after approximately 200 cycles?**
  - Thank you for the question. The study was part of our full cell study and evaluating how the irreversible capacities associated with silicon gradually raise the opening voltage of the cathode by gradually shifting the operation plateaus to maintain the cell voltage. As the anode gradually loses lithium to side reactions, the cathode uses more lithium to maintain voltage. This shift then gradually raises the anode voltage, and since the graphite insertion voltage is lower, the graphite slowly ceases participating in the cell reaction. Previously Johnson and Dose also showed that if against a lithium anode, the graphite capacity is maintained. The overlap of the capacities after 200 cycles is a consequence of the higher impedance of the higher content silicon cells evaluated. This is also being addressed as a CAMP milestone for FY20.
- **Several reviewers were concerned the program as described will not rule out components but continue in an exploratory manner**
  - Thank you for the question. A multi-lab effort was set up (organized initially thru CAMP) to build a baseline system by choosing the best available materials and components then, while evaluating other materials, update the baseline cell chemistry on a regular basis. Earlier work identified a baseline silicon and we are on the third generation of silicon suppliers based on advances in morphology, processing, and coatings. We have moved from Gen2/FEC to Gen 2/FEC/additives for electrolytes while still evaluating the LHCE systems. Surface coatings have gone from simple silica natural passivation to functionalized organic layers, although due to scaling this has not yet displaced baseline Si from Paraclete. At the electrode level, in FY18 we went from silicon-graphite composites to high silicon after identifying several issues with surface binder chemistry that were detrimental to cycle life. As the effort advances, discoveries are made are evaluated and either added to the baseline or sent back for additional studies. Requirements for full cell evaluation with cell level goals have been added to the effort as Q4 end of year milestones.

Contributors and Acknowledgment

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Contributors

- Daniel Abraham
- Shabbir Ahmed
- Eva Allen
- Ira Bloom
- Su Ahmed
- Beth Armstrong
- Ryan Armstrong
- Katie Browning
- M. Katie Burdette-Trofimov
- Anthony Burrell
- Saida Cora
- Jaclyn Coyle
- Yanjie Cui
- Dennis Dees
- Fulya Dogan
- Alison Dunlop
- Yeyoung Ha
- Sang-Don Han
- Emma Hopkins
- Andrew Jansen
- Sisi Jiang
- Haiping Jia
- Christopher Johnson
- Baris Key
- Robert Kostecki
- Joseph Kubal
- Bob Jin Kwon
- Xiang Li
- Xiaolin Li
- Chen Liao
- Min Ling
- Michael Liu
- Gao Liu
- Wenquan Lu
- Hannah Morin
- Nate Neale
- K. Nie
- Bryant Polzin
- Andressa Rodriguez Prado
- Marco-Tulio F. Rodrigues
- Alexander Rogers
- Niya Sa
- Yangping Sheng
- Seoung-Bum Son
- Caleb Stetson
- Wei Tong
- Stephen Trask
- Ritesh Uppuluri
- Jack Vaughey
- Gabriel Veith
- Johanna Weker
- Qingliu Wu
- Yimin Wu
- Zhen Zhen Yang
- Kang Yao
- Ji-Guang Zhang
- Lu Zhang
- John Zhang
- Sanpei Zhang
- Tianyue Zheng
- Ting Zhang

Research Facilities

- Cell Analysis, Modeling, and Prototyping (CAMP)
- Spallation Neutron Source (SNS)
- Battery Abuse Testing Laboratory (BATLab)
- Post-Test Facility (PTF)
- SLAC National Accelerator Laboratory

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Remaining Challenges and Barriers

- The focus of the Deep Dive effort has been on electrode level and cell level studies of silicon – based electrodes. We have efforts looking to understand the **surface/electrolyte reactivity** and their relationship to coulombic efficiency/cycle life, **SEI stability** in an electrochemical cell, **electrode formulations**, and other aspects of cell design and analysis

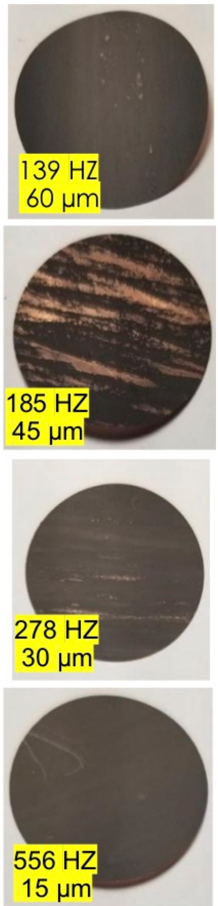
- ORNL has highlighted the segregation of binder on electrode formation as a cause of diminished electrode performance. Better processing routes or processes need to be explored.
- Developing more in-depth cost Si-specific models in association with the BatPaC techno-economic modeling group
- SEI stability in systems that incorporate an alkaline metal salt (Zintl) additive shows significant improvement over baseline; on long term cycling it appears to diminish its effectiveness as the cation diffuses away from the surface. Methods to make the species less mobile would improve long term effectiveness.

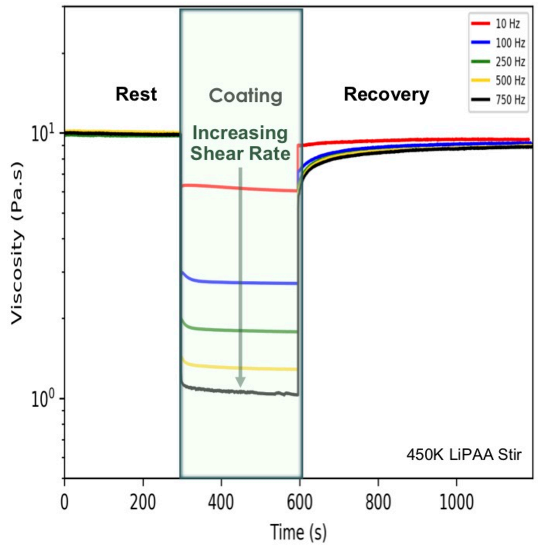
Proposed Future Research

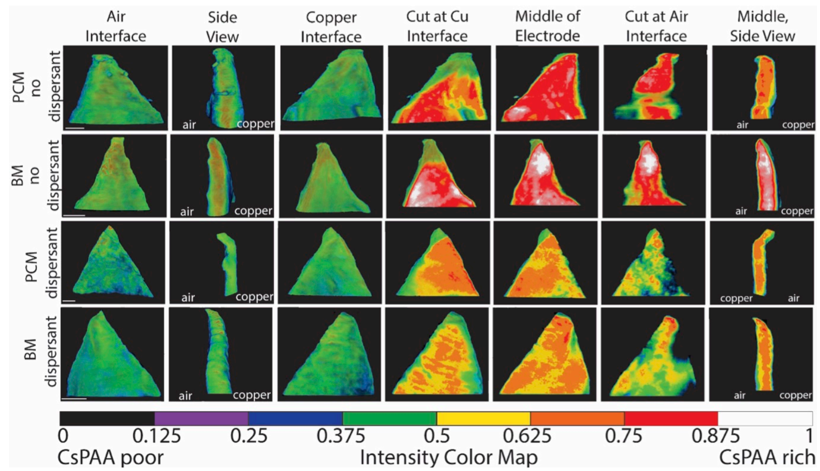
- Experimentally validated control of processing parameters to yield reproducible, reliable, and stable electrodes.
  - Understanding of rheology and impact on formulation and performance
  - Devise and create new interfacial modifications of the silicon surface that add stability and performance to the electrode structure
  - Continuous feedback to team doing fundamental work
  - Devise new processing strategies while utilizing advanced characterization techniques to see how changes to the electrode structure can be detected, modeled, and understood to improve performance.

Any proposed future work is subject to change based on funding levels

Summary





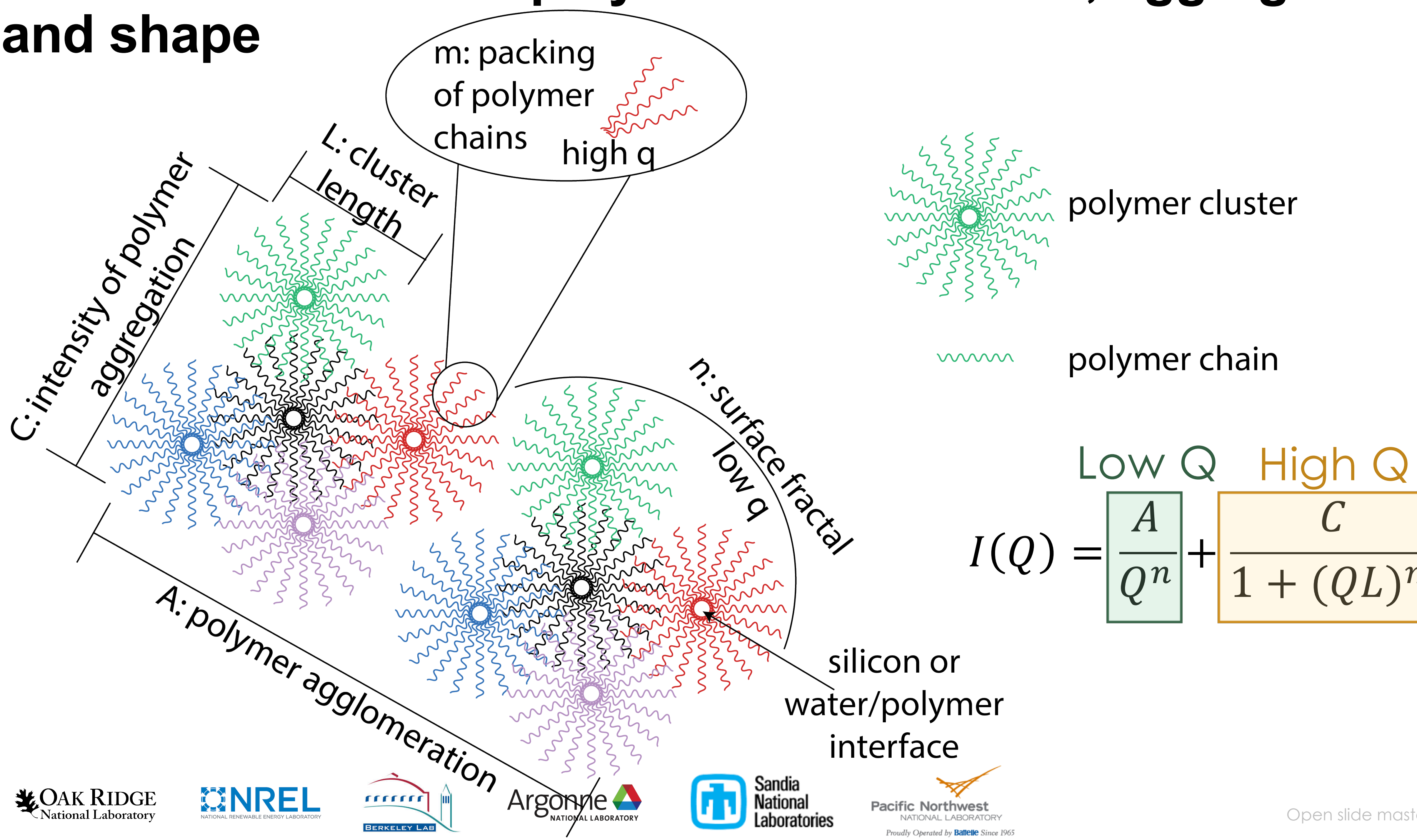


Stress during casting is directly related to electrode homogeneity

Carbon black segregation needing optimization. Mixing and slurry chemistry provides a pathway to improve electrode homogeneity

Technical Back Up Slides

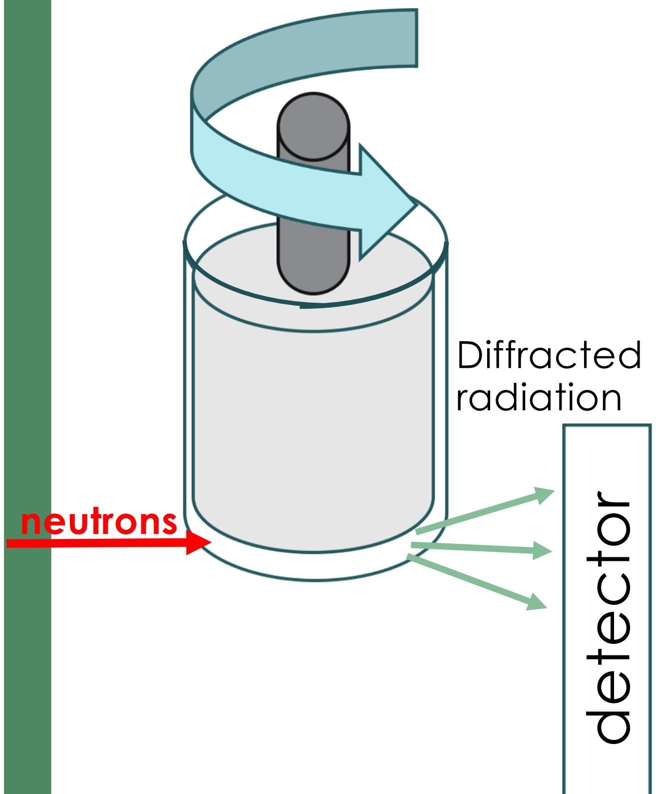
USANS can show us polymer conformation, aggregation, and shape

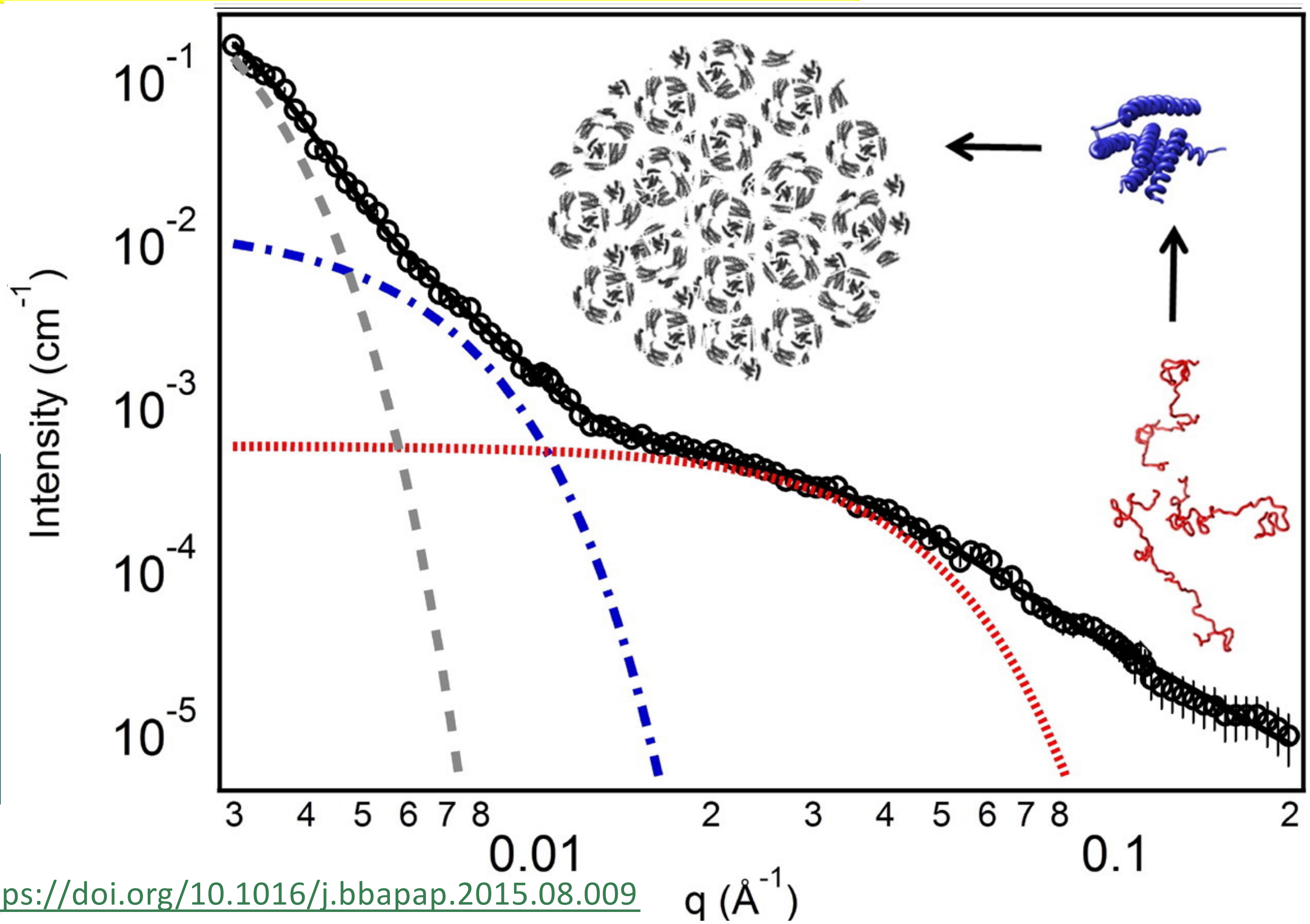


$$I(Q) = \boxed{\frac{A}{Q^n}} + \boxed{\frac{C}{1+(QL)^m}} + B$$

USANS shows sizing on multiple length scales

Ultra-small angle neutron scattering





https://doi.org/10.1016/j.bbapap.2015.08.009

How is nanotomography performed?